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(54) Title: METHOD OF MAKING BUILDING BLOCKS FROM COAL COMBUSTION WASTE AND RELATED PRODUCTS

(57) Abstract

A method of making a building block from coal combustion products, such as fly ash and bottom ash includes employing a major amount of such ash in combination with a calciferous additive and water to cure and shape the same under the influence of controlled pressure and temperature for a predetermined time to create building block which is characterized by a mineralogical crystalline phase. Preferred ratios of fly ash to bottom components are disclosed. The product produced by the method is also disclosed.

METHOD OF MAKING BUILDING BLOCKS FROM COAL COMBUSTION WASTE AND RELATED PRODUCTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an improved method for the manufacture of shaped building blocks from selected coal combustion wastes and related products. More specifically, the invention relates to a method for producing high strength building blocks of precise dimensions and desired properties from coal combustion fly ash and bottom ash and related products.

2. Description of the Prior Art

Due to the rapidly diminishing availability of suitable landfill space and the escalating cost of land disposal, the daily generation of large volumes of coal combustion wastes at coal-fired power plants has created a costly disposal problem for electric utility companies throughout the world. Accordingly, power companies operating such plants have intensified their efforts to find high volume, income producing, commercial uses for coal combustion fly ash and bottom ash that provide economical alternatives to landfill disposal of these wastes.

There currently exists a number of known commercial uses for coal combustion fly ash and bottom ash as substitute materials in the production of low strength cementicious products. In one such use, the pozzolanic properties of fly ash have established this waste product as a substitute for Portland cement in the production of concrete. The widespread use of fly ash in this application, however, requires that the carbon content of the ash be less than 3% by weight. The utilization of fly ash as a constituent in concrete is disclosed in United States Patents 4,115,256, 4,121,945, 4,453,978, 4,517,078, 5,160,559, and 5,227,047, which disclose various means, including combustion, electrostatic, magnetic, air classification, and flotation means, for removing carbon from fly ash or chemical means to neutralize the negative effect of carbon on the properties of the concrete. As a result, the requirement for such reduced carbon content involves additional processing of the fly ash and undesirable associated capital investment and processing costs.

It is obvious from the foregoing disclosures that, in order to utilize large volumes of fly ash on a continuing basis, a commercial application must be found in which the carbon content of the fly ash has a less adverse effect upon the properties of

the product in which it is incorporated. One such application, disclosed in United States Patent 5,211,750, involves combining fly ash with flue gas desulfurization sludge, lime, and water, and compacting the resulting mixture into a shaped cementiciously-bonded product that is subsequently cured and crushed to yield an aggregate having a compressive strength in the range of 1,000-4,000 psi.

Another known method for utilizing fly ash as a constituent in a shaped cementiciously-bonded product, disclosed in United States Patent 4,397,801, involves mixing (a) pulverized fly ash, (b) a spent fluidized bed combustion residue containing limestone particles and oxidic sulfur compounds, and (c) water, with or without the addition of Portland cement. The mixture is compacted to form a shaped masonry block which is subsequently crushed to create an aggregate used as a constituent in concrete, mortar mixes, and road base materials. The shaped masonry block produced prior to crushing is said to have exhibited compressive strengths that varied over time. The strengths were said to increase from 770-1,970 psi seven days after compacting to 1,570-2,950 psi twenty-eight days after compacting. Such strength levels are well below those required for high strength structural building bricks and blocks. United States Patent 5,350,549 also discloses combining fly ash with spent fluidized bed material to form a shaped cementiciously-bonded composition. In this case, an aggregate is produced by curing the formed shape under ambient conditions while saturating the shape with water.

In yet another method for producing cementiciously-bonded construction products from coal combustion wastes, disclosed in United States Patent 5,362,319, fly ash or bottom ash, with or without the addition of at least one other component selected from the group consisting of papermill waste, lime, clay, Portland cement, or plaster of paris, is mixed with a strong oxidant to produce a shaped body that is allowed to harden and strengthen over time at ambient conditions.

A method of producing a stabilized cementiciously-bonded building block from both fly ash and bottom ash is discussed in United States Patent 5,358,760. In this method, fly ash and bottom ash are combined with gypsum, lime, and calcium carbonate. The resulting admixture is formed into a block under a compressive force; and the block is allowed to cure under ambient conditions without the application of external heat. Construction blocks produced in this manner were said to exhibit a compressive strength of only 1,341 psi.

Another known method of utilizing both fly ash and bottom ash to produce shaped cementiciously-bonded structural products, disclosed in United States Patents 5,374,307 and 5,366,548, involves adding water to a mixture of fly ash and bottom ash, which may or may not contain one or more additional waste products or sand or clay, and compressing the moistened mixture at a pressure in the range of 1,000 to 2,500 psi to form a molded body which is said to subsequently cure and strengthen at ambient conditions. Structures produced in this manner generally exhibited compressive strengths in the range of 1,900-3,600 psi.

These prior art disclosures produce shaped construction products that exhibit relatively low compressive strengths that increase slowly with time to ultimate levels that are inadequate for the use of these products as high-strength building brick or block. This lack of strength is believed to be due, primarily, to insufficient crystal formation and growth caused by curing the formed structures at ambient conditions, and the lack of control of temperature, pressure, humidity, and time during the curing process. The absence of significant crystal growth prevents the formation of a strong interlocking crystalline matrix. A typical cementiciously-bonded structure is that of a standard concrete building block. A structure of this type, which is typified by the lack of significant crystal formation and growth and the absence of a high strength interlocking crystalline matrix, normally yields a compressive strength of less than 3,500 psi. Such a structure, magnified 2,000 times, is shown in the photomicrograph of Figure 1.

High strength, crystalline-bonded shaped building products produced from naturally-occurring materials, and methods for their manufacture, are known in the art. Calcium silicate bricks, produced essentially from sand and lime and intended for use in brick masonry applications, are disclosed in the American Society For Testing Materials specification ASTM C73-94a. Shaped building bricks and blocks of this type are produced on a commercial basis by Schneider Kalkandsteine GmbH in Germany and a number of other companies in Europe. Such bricks and blocks are known to be widely used in residential and commercial building construction in Germany, the Netherlands, and Russia.

Calcium silicate bricks are normally produced by mixing 85%-96% sand, 3%-8% lime, and up to 10% water, compacting the mixture to form a shaped body, and curing said body at an elevated temperature in pressurized steam for a time sufficient to

allow the formation and growth of calcium silicate crystals. The compacting pressure employed normally ranges from 2,500 psi to 10,000 psi. Curing is normally accomplished by autoclaving the shaped bodies in an atmosphere of saturated steam at a temperature in the range of 180°C to 220°C and a pressure in the range of 200 psi-300 psi for a period of 4 to 6 hours.

Calcium silicate bricks produced from naturally-occurring materials under such conditions are reported to exhibit compressive strengths ranging up to 8,000 psi ("The Chemistry of Cements," Taylor, H.F.W., Academic Press). This dramatic improvement in strength has been attributed to the formation of a ubiquitous strong, interlocking crystalline matrix that tightly binds the mineral particles in the structure. It has been reported that the calcium silicate crystal phase most responsible for imparting strength to the interlocking crystalline matrix is Tobermorite, a hydrated calcium silicate species (Mortel, H., "Mineral Composition, Microstructure, and Physical Properties of Calcium Silicate Bricks," Fortschritte der Mineralogie, 58, pp 37-67, 1980). The structure (magnified 2,000 times) of a typical commercial calcium silicate building product manufactured from naturally-occurring materials showing the interlocking Tobermorite crystal matrix responsible for strengthening, is illustrated in the photomicrograph in Figure 2.

The combination of compacting and steam-curing has also been used to produce high strength shaped building products from man-made wastes, such as copper mine tailings, zinc mine tailings, asbestos fines, and roofing granules (United States Department of the Interior, Bureau of Mines, Report of Investigation 7856, "Steam-Cured Bricks From Industrial Mineral Wastes," 1974). Building bricks of this type, produced by blending one of the aforementioned mineral wastes with calcium hydroxide or Portland cement, and compacting and steam-curing under conditions similar to those used to produce bricks from naturally-occurring minerals, are said to exhibit compressive strengths similar to those heretofore reported for bricks produced from naturally-occurring minerals.

Crystalline-bonded construction products incorporating coal combustion wastes and methods for their manufacture are also known in the art.

United States Patent 4,683,006 discloses a low strength, crystalline-bonded shaped construction aggregate produced by mixing pulverized fly ash with lime, shaping

the mixture, and curing the shaped mixture in a moisture-controlled atmosphere at temperatures in the range of 35°C and 80°C. The strength of the resultant shaped body is attributed to a pozzolanic bond that includes mechanical bonds formed by crystallites of Ettringite and amorphous calcium silicate, calcium aluminate, or calcium aluminum silicate, or mixtures thereof. The compressive strength of the shaped bodies so formed was said to be less than 100 psi.

The use of fly ash as a partial substitute for sand in the production of calcium silicate-type brick has previously been reported in "Sand Fly-Ash Bricks," Materials Research Standards, USA (1964) and in Report 18 of the Research Association of Calc Sandstone (Germany), "The Use of Industrial Waste Products, Their Influence On The Characteristics Of Calc Sandstone," Part II, Hard Coal Filter Ash, May 1970.

None of these prior art processes, or any product resulting therefrom, is adapted to utilize larger volumes of coal combustion wastes in the manufacture of shaped building products nor to significantly reduce the volume of coal combustion fly ash and bottom ash currently being disposed in landfills by permitting large volumes of such wastes to be utilized as the major raw material components in the manufacture of high strength shaped construction products. There remains, therefore, a need for a practical method for the manufacture of high strength, crystalline-bonded building bricks and blocks composed primarily of coal combustion fly ash and bottom ash. A process capable of producing such bricks and blocks would substantially reduce the need for landfill disposal of these wastes and be of great economic value to operators of coal combustion power plants.

SUMMARY OF INVENTION

The present invention has met the hereinabove described needs. The invention provides a method for producing high strength shaped construction products composed primarily of a combination of coal combustion wastes. The method preferably involves the production of building brick and block by combining coal combustion fly ash and bottom ash with an additive that enhances the formation of mineralogically-based crystals and forming and curing the brick and block under conditions that result in the formation of a stable interlocking crystalline matrix that imparts the desired structural strength and stability to said brick and block.

In a preferred practice of the method of the invention, a calciferous additive, such as lime, may be employed as the additive and water is blended into the

mixture. Curing is preferably effected at elevated temperature and pressure for a predetermined period of time to produce the desired mineralogical crystalline phase. Certain preferred ratios of fly ash to bottom ash are provided. The invention also provides a related product.

It is an object of the present invention to provide a high strength, structurally stable shaped building product consisting essentially of coal combustion fly ash and bottom ash and an economical, efficient method for its manufacture.

It is another object of the invention to provide such a high strength, structurally stable shaped building product in which the high strength and structural stability are imparted by an interlocking crystalline matrix that intimately bonds the fly ash and bottom ash particles within the product structure.

It is a further object of the invention to provide such a high strength, structurally stable shaped building product in which the interlocking crystalline matrix is achieved by making said product under controlled conditions of elevated temperature, pressure, and humidity.

It is a further object of the invention to provide a method of making a high strength, structurally stable shaped building product consisting essentially of coal combustion fly ash and bottom ash which product is strengthened by an interlocking crystalline matrix in which said matrix consists primarily of hydrothermally-grown Tobermorite crystals.

It is a further object of the invention to provide a high strength shaped man-made building product in which the major ingredients are man made and the adverse effects of impurities on mechanical properties are significantly reduced.

It is a further object of the invention to provide a method of making a precisely shaped building product from a mixture of coal combustion fly ash and bottom ash by applying pressure to said mixture in a mold of the desired shape.

It is a further object of this invention to provide a method of making a load bearing building product of improved quality and consistency.

It is yet another object of the invention to provide such a method and a related product which can be made without requiring reduction in the carbon content of the fly ash.

These and other objects of the invention will be more fully understood from the following detailed description of the invention on reference to the figures appended hereto.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a photomicrograph showing a prior art structure, at a magnification of 2,000X, of a cementiciously-bonded shaped concrete building product.

FIG. 2 is a photomicrograph showing a prior art structure, at a magnification of 2,000X, of a crystalline-bonded shaped building product manufactured from naturally-occurring sand and lime.

FIG. 3 is a photomicrograph showing the structure, at a magnification of 2,000X, of a crystalline-bonded shaped building product produced from coal combustion fly ash and bottom ash in accordance with the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

As employed herein, the terms "building blocks" or "building bricks" are employed interchangeably and shall mean structural building blocks or bricks of predetermined shape or size, a plurality of which are adapted to be employed in an assembled array in walls, in roads or walkways, and related building product and non-building product uses, or aggregate pieces, regardless of whether the blocks or bricks are load bearing or not and regardless of whether they have rectangular faces or not.

The present invention is applicable to the production of a broad spectrum of shaped building blocks or bricks from a mixture comprised essentially of particulate coal combustion wastes and an additive that reacts with such wastes to form a ubiquitous crystalline matrix that tightly binds said individual waste particles into a strong, coherent, stable structure.

The invention provides a method of (a) combining particulate siliceous coal combustion fly ash and bottom ash with a calciferous additive, (b) blending the resulting ash/additive mixture with water, (c) compacting the moistened mixture into the desired shape at a pressure sufficient to attain intimate contact among the fly ash, bottom ash, and additive particles, and (d) curing said compacted shape under conditions of elevated temperature and pressure in a moisture laden atmosphere for sufficient time to permit nucleation and growth of an interlocking crystalline matrix comprised essentially of hydrothermally-formed calcium silicate-based crystals that imparts structural strength and stability to said cured shape.

Structural analyses, performed by means of scanning electron microscopy (SEM) and x-ray diffraction (XRD), of a shaped building blocks produced in accordance with the method of this invention, indicate that the strength and stability of said building product is effected by an interlocking matrix of calcium silicate crystals of the Tobermorite ($Ca_5Si_6O_{17}•5H_2O$) species or variations thereof. The SEM photomicrograph illustrating the structure (magnified 2,020X) of such a product, shown in FIG. 3, reveals the interlocking crystallite matrix 1 connecting and tightly binding the fly ash particles 2 and the bottom ash particles 3 in the structure, thereby imparting structural strength and stability to the resultant product.

FIG. 3 also shows that the fly ash particles 2 and bottom ash particles 3 in the structure are coated with a layer of hydrous calcium silicate 4 from which individual Tobermorite crystals 6 nucleate and grow. Impurity particles 5 in the structure, including ferritic and carbonaceous particles, are similarly coated with a layer of hydrous calcium silicate. The presence of such coatings on the surface of the impurity particles render such particles inert and minimize any negative effect that the particles might have on the strength and stability of the cured structural shape.

The preferred method of the invention involves procedures that maximize the level of particle coating, significantly increase the degree of particle-to-particle contact in the mass, and maximize the extent of Tobermorite crystallite nucleation and growth within the structure. These preferred method steps include, but are not limited to, optimization of (a) the proportion of fly ash:bottom ash in the mixture and the particle size distribution resulting therefrom, (b) the type and amount of calciferous additive employed, (c) the quantity of water added to the ash/additive mixture, (d) the pressure used to form the desired shape, and (e) the temperature, pressure, humidity, and time employed during curing of the formed shape.

Suitable high strength shaped building products can be produced in accordance with the present invention from commercially-generated coal combustion fly ash and bottom ash without requiring reduction in carbon content in the ash. Examples of suitable particle size distributions are shown in Table 1.

TABLE 1

U.S. Mesh Size	Fly Ash (Wt.%)	Bottom Ash (Wt%)
-10 + 45	0	0
-45 + 70	1.25	25.0
-70 +100	2.16	35.0
-100	96.59	40.0

Shaped building products having mechanical properties equivalent to those of conventional building brick and block can be produced from mixtures of coal combustion fly ash and bottom ash in which the ratio of fly ash to bottom ash varies over a wide range. Specifically, for shaped building products ranging in size from a cylinder of about 1.3" diameter (D) x 1" length (L) to a product having six rectangle faces and a size of about 4" length (L) x 1.8" width (W) x 0.8" thickness (T) produced from fly ash and bottom ash of the aforementioned particle size distributions, preferred mechanical properties can be achieved when the ratio of fly ash to bottom ash is in the range of about 1 part fly ash:4 parts bottom ash to about 1 part fly ash:1 part bottom ash by weight. Lesser, but acceptable mechanical properties can be achieved when fly ash to bottom ash ratios of about 3:2 to about 4:1 by weight are employed. The properties attained are still suitable for numerous building applications. Accordingly, a suitable broad range for the fly ash:bottom ash ratio in such products is about 1 part fly ash:4 parts bottom ash to about 4 parts fly ash:1 part bottom ash; with a preferred range being about 1 part fly ash:4 parts bottom ash to about 1 part fly ash:1 part bottom ash. The most preferred ratio is about 1 part fly ash:4 parts bottom ash. All references in the ratios are by weight.

As the dimensions of prior art cementiciously-bonded and silicate crystal-bonded shaped structural products increase, the proportion of coarse particles utilized in their manufacture must be increased to maintain a specific strength level in the product. The method of the present invention may be employed to manufacture large shaped building blocks by increasing the weight of coarse bottom ash in the mixture to levels greater than that in the preferred ratio of 1 part fly ash:4 parts bottom ash and/or increasing the average particle size in said bottom ash.

It has also been found that the optimum combination of strength and structural integrity may be achieved in shaped building blocks manufactured in accordance with this invention when the amount of the calciferous additive, which may be in the form of hydrated lime [$CaO \bullet H_2O$] or quicklime [CaO], in the ash/additive mixture is maintained in the range of 5% to 15% by weight, and preferably in the range of 10% to 12% by weight of the mixture. It has also been determined that superior properties are achieved when the free water added to the mixture prior to shaping is maintained in the range of 5% to 15% by weight of the mixture including the water. When quicklime is substituted for hydrated lime, the amount of free water added to the mix is preferably increased by an amount equal to the amount of water required to hydrate the quicklime.

To maximize particle-to-particle contact within the shaped building block of the invention, crystal growth during hydrothermal treatment, and the compressive strength of the resultant product, it is preferred that the moistened mixture be shaped shortly after blending by compacting the mixture at a pressure in the range of 5,000 psi to 10,000 psi in a mold cavity having the desired shape. A compacting pressure of about 7,000 to 8,000 psi is preferred. Dwell time at pressure normally ranges from about 1 second to 3 minutes. Shaped building products compacted in this manner normally have an as-compacted density in the range of about 1.5 grams/cubic centimeter to 2.0 grams/cubic centimeter.

Hydrothermal curing of the compacted shape is preferably achieved by curing the as-compacted shape in a saturated steam atmosphere at a temperature ranging from 180°C to 220°C at a pressure between 150 psig and 340 psig for a period of 4 to 8 hours in an autoclave or similar apparatus. In order to maximize Tobermorite crystallite nucleation and growth and create the optimum interlocking Tobermorite crystallite matrix within the structure during curing, it is preferred that the shape be cured at about 190°C to 210°C for about 5 to 7 hours at a pressure of about 220 to 260 psig.

A comparison of relative peak intensities of X-ray diffraction (XRD) patterns obtained from shaped products produced from a mixture of about 1 part fly ash and about 4 parts bottom ash by weight processed in accordance with the method of the invention and cured at temperatures of 160°C, 200°C, and 225°C, provided in Table 2. The data in Table 2 shows that, using the peak intensities of the product cured at 160°C normalized to unity as the basis of comparison, the relative peak intensity of the

Tobermorite phase in the structure of the product cured at 225°C increased significantly (538%) relative to peak intensity of the Tobermorite phase in the structure of the product cured at 160°C whereas the peak intensities of the other mineral species present in the products either decreased or increased less than 23% under similar conditions. While the relative peak intensity of XRD patterns is not directly proportional to an increase in mass of a species in a structure, these data indicate a significant increase in the amount and crystallinity of the Tobermorite phase in the structures cured at the higher temperatures and confirms the correlation between Tobermorite crystal formation and increased strength in the product.

TABLE 2

MINERAL SPECIES	RELATIVE XRD PEAK INTENSITY @ 160°C CURE	RELATIVE XRD PEAK INTENSITY @ 200°C CURE	RELATIVE XRD PEAK INTENSITY @ 225°C CURE	% INCREASE IN RELATIVE XRD PEAK INTENSITY BETWEEN 160°C AND 225°C CURES
QUARTZ	1	1.14	0.91	- 9 %
MULLITE	1	1.25	1.16	+ 16 %
TOBERMORITE	1	4.17	5.38	+ 538 %
CALCIUM ALUMINUM SILICATE HYDROXIDE	1	0.47	0.66	- 34 %
CALCITE	1	0.67	0.95	- 5 %
PORTLANDITE	1	0.18	0.40	- 60 %
HEMATITE	1	1.30	1.22	+ 22 %

Shaped building blocks produced in accordance with the method of the invention normally possess an internal structure similar to that shown in FIG. 3, a cured density in the range of about 95 pounds/cubic foot to 130 pounds/cubic foot, a compressive strength ranging from about 2,000 psi to 8,500 psi and water absorbtivity of about 15% to 20%. Table 3 compares certain properties and characteristics of shaped building blocks of the present invention with those of conventional prior art clay

building brick and concrete building block. The properties of the shaped building block produced in accordance with the method of the invention have mechanical properties which compare favorably with those of the prior art which are used as building bricks and blocks.

TABLE 3

PROPERTY	PRODUCT OF INVENTION	RED CLAY BUILDING BRICK	CONCRETE BUILDING BLOCK
DENSITY (LB/CU FT)	95 - 130	90 - 150	110 - 140
COMPRESSIVE STRENGTH (PSI)	2,000 - 8,500	1,500 - 12,000	1,000 - 5,000

The following examples provide specific preferred practices in employing the method of the invention.

EXAMPLES

The examples provided herein verify that shaped building bricks or blocks manufactured in accordance with the method of the present invention exhibit properties and characteristics that make said products suitable for use in residential and commercial building construction and, as shown by the data in Table 3, are viable alternatives to conventional prior art clay building bricks and concrete block.

EXAMPLE 1

In this example, 1.3" D x 1" L cylindrically shaped bodies were produced by (a) mixing 60 grams of fly ash and 240 grams of bottom ash, both commercially generated by a coal burning electric utility and both having particle size distributions falling generally within those recited in Table 1 hereof, to achieve a 1:4 ratio of fly ash:bottom ash; (b) adding 39 grams of hydrated lime to achieve a lime content in the total ash-lime mixture of 11.5% by weight; (c) adding 30 grams of free water to the ash-lime mixture to achieve a total water content in the moistened mixture of 8.1% by weight; (d) blending the moistened mixture to achieve uniformity; (e) compacting the moistened mixture to the aforesaid cylindrical shape by application of pressure at a level of 10,000 psi and maintaining the compact under said pressure for a period of 3

minutes; and (f) curing the compacted shape in a saturated steam atmosphere in an autoclave at a temperature of 200°C and a pressure of 240 psig for a period of 6 hours.

The compressive strength of the shaped products so produced, determined in accordance with ASTM Test Method C67 seven days after curing, was 6,325 psi, thereby demonstrating that the compressive strength of shaped products based upon a fly ash:bottom ash ratio of 1:4 and produced in accordance with the method of the invention is suitable for building construction applications and competitive with that of clay building brick.

EXAMPLE 2

In this example, 1.3 " D x 1" L cylindrically shaped bodies were produced by (a) mixing 120 grams of fly ash and 180 grams of bottom ash, both commercially generated by a coal burning electric utility and both having particle size distributions falling generally within those recited in Table 1 hereof, to achieve a 2:3 ratio of fly ash:bottom ash by weight; (b) adding 30 grams of hydrated lime to achieve a lime content in the total ash-lime mixture of 9.1% by weight; (c) adding 30 grams of free water to the ash-lime mixture to achieve a total water content in the moistened mixture of 8.3% by weight; (d) blending the moistened mixture to achieve uniformity; (e) compacting the moistened mixture to the aforesaid cylindrical shape by application of pressure at a level of 7,500 psi and maintaining the compact under said pressure for a period of 2 minutes; and (f) curing the compacted shape in a saturated steam atmosphere in an autoclave at a temperature of 200°C and a pressure of 240 psig for a period of 2 hours.

The compressive strength of the shaped products so produced, determined in accordance with ASTM Test Method C67 seven days after curing, was 5,767 psi thereby demonstrating that the compressive strength of shaped products based upon a fly ash:bottom ash ratio of 2:3 and produced in accordance with the method of the invention is suitable for building construction applications and competitive with that of clay building brick.

EXAMPLE 3

In this example, 1.3" D x 1" L cylindrically shaped bodies were produced by (a) mixing 156 grams of fly ash and 144 grams of bottom ash, both commercially generated by a coal burning electric utility and both having particle size distributions generally falling within those recited in Table 1 hereof, to achieve a 1.08:1 ratio of fly ash:bottom ash; (b) adding 39 grams of hydrated lime to achieve a lime content in the total ash-lime mixture of 11.5% by weight; (c) adding 30 grams of free water to the ash-lime mixture to achieve a total water content in the moistened mixture of 8.1% by weight; (d) blending the moistened mixture to achieve uniformity; (e) compacting the moistened mixture to the aforesaid cylindrical shape by application of pressure at a level of 7,500 psi and maintaining the compact under said pressure for a period of 2 minutes; and (f) curing the compacted shape in a saturated steam atmosphere in an autoclave at a temperature of 200°C and a pressure of 240 psig for a period of 6 hours.

The compressive strength of the shaped products so produced, determined in accordance with ASTM Test Method C67 seven days after curing, was 6,840 psi, thereby demonstrating that the compressive strength of shaped products based upon a fly ash:bottom ash ratio of essentially 1:1 and produced in accordance with the method of the invention is suitable for building construction applications and competitive with that of clay building brick.

EXAMPLE 4

In this example, 1.3" D x 1" L cylindrically shaped bodies were produced by (a) mixing 180 grams of fly ash and 120 grams of bottom ash, both commercially generated by a coal burning electric utility and both having particle size distributions generally falling with those recited in Table 1 hereof, to achieve a 3:2 ratio of fly ash:bottom ash; (b) adding 30 grams of hydrated lime to achieve a lime content in the total ash-lime mixture of 9.1% by weight; (c) adding 30 grams of free water to the ash-lime mixture to achieve a total water content in the moistened mixture of 8.3% by weight; (d) blending the moistened mixture to achieve uniformity; (e) compacting the moistened mixture to the aforesaid cylindrical shape by application of pressure at a level of 10,000 psi and maintaining the compact under said pressure for a period of 2 minutes; and (f) curing the compacted shape in a saturated steam atmosphere in an autoclave at a temperature of 200°C and a pressure of 240 psig for a period of 6 hours.

The compressive strength of the shaped products so produced, determined in accordance with ASTM Test Method C67 seven days after curing, was 3,233 psi, thereby demonstrating that the compressive strength of shaped products based upon a fly ash:bottom ash ratio of 3:2 and produced in accordance with the method of the invention is suitable for construction applications and competitive with that of concrete building block.

EXAMPLE 5

In this example, 1.3" D x 1" L cylindrically shaped bodies were produced by (a) mixing 240 grams of fly ash and 60 grams of bottom ash, both commercially generated by a coal burning electric utility and both having particle size distributions generally falling within those recited in Table 1 hereof, to achieve a 4:1 ratio of fly ash:bottom ash; (b) adding 30 grams of hydrated lime to achieve a lime content in the total ash-lime mixture of 9.1% by weight; (c) adding 30 grams of free water to the ash-lime mixture to achieve a total water content in the moistened mixture of 8.3 % by weight; (d) blending the moistened mixture to achieve uniformity; (e) compacting the moistened mixture to the aforesaid cylindrical shape by application of pressure at a level of 10,000 psi and maintaining the compact under said pressure for a period of 2 minutes; and (f) curing the compacted shape in a saturated steam atmosphere in an autoclave at a temperature of 200°C and a pressure of 240 psig for a period of 6 hours.

The compressive strength of the shaped products so produced, determined in accordance with ASTM Test Method C67 seven days after curing, was 3,733 psi, thereby demonstrating that the compressive strength of shaped products based upon a fly ash:bottom ash ratio of 4:1 and produced in accordance with the method of the invention are suitable for building construction applications and competitive with that of concrete building block.

A comparison of the compressive strengths of the 1:4, 2:3, 1:1, 3:2, and 4:1 Fly Ash:Bottom Ash samples with those specified for prior art clay building brick and concrete block construction products is presented in Table 4. This confirms the compressive strength of the building blocks of the present invention being well within the accepted prior art brick and block compressive strength ranges.

TABLE 4

MATERIAL	AVERAGE COMPRESSIVE STRENGTH @ 7 DAYS AFTER CURING (PSI)
1:4 FLY ASH:BOTTOM ASH	7,340
2:3 FLY ASH:BOTTOM ASH	5,767
1:1 FLY ASH:BOTTOM ASH	6,840
3:2 FLY ASH:BOTTOM ASH	3,233
4:1 FLY ASH:BOTTOM ASH	3,733
CLAY BRICK	1,500 - 12,000
CONCRETE BLOCK	1,000 - 5,000

The invention is also adapted to provide colored building bricks, if desired. Shaped building bricks having colors of a permanent nature that differ from the gray color normal to products produced from a mixture of fly ash and bottom ash can be produced in accordance with this invention by incorporating into the mixture either prior to blending with water, as is preferred, or prior to compacting naturally colored mineralogical components into the fly ash:bottom ash mix. For example, red bricks have been produced by adding about 2-3% by weight of hematite to a 1:4 fly ash:bottom ash ratio mixture. Black bricks can be produced by adding magnetite to the blend. Bricks exhibiting other permanent colors can be produced by adding a mineralogical compound of the desired color to the desired fly ash:bottom ash mixture. The shade and intensity of the color is dependent upon the amount of colored mineral employed.

For convenience of disclosure. the disclosure herein has made reference to specific compositions, particle size distributions, processing parameters. and product configurations. It will be obvious to those skilled in the art that one may practice the invention employing other compositions. particle size distributions. processing parameters, and product configurations.

While. for convenience of disclosure. the above discussion and illustrations have made reference to the use of lime. it will be obvious to those skilled in the art that calcium-containing flue gas desulfurization sludge or similar materials can also be used as a source of calcium.

While the discussion herein has made reference to shaped building products such as building brick and block. it will be apparent to those skilled in the art that one may practice the invention to produce shaped construction aggregate and shapes for non-construction purposes.

It will be appreciated that the method of this invention provides a cost effective means for producing commercially viable strong, stable shaped building bricks or blocks from coal combustion wastes without requiring reduction in carbon content thereof. The increased commercial use of such wastes resulting from this invention will significantly reduce the volume of coal combustion wastes that must be disposed of in landfills. The utilization of this invention to achieve this end is. therefore of great environmental benefit to society.

Whereas particular embodiments of the invention have been described herein for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details may be made without departing from the invention as defined in the appended claims.

CLAIMS:

1. A method of making a shaped product comprising

admixing a major portion by weight of a coal combustion ash with a calciferous additive in proportions which establish a mineralogical crystalline phase.

blending water with said mixture to create a moistened blend.

forming said moistened blend into a shaped product by compacting it at pressures in excess of about 5,000 psi, and

hydrothermally treating said shaped product to facilitate the formation of interlocking mineralogical crystals therein.

2. The method of claim 1 including

employing as said coal combustion ash a mixture of fly ash and bottom ash.

3. The method of claim 2 including

employing on a weight basis said fly ash in a ratio to bottom ash of about 1 to 4 to about 1 to 1.

4. The method of claim 2 including

employing on a weight basis said fly ash in a ratio to bottom ash of about 3 to 2 to about 4 to 1.

5. The method of claim 3 including

employing as said calciferous additive a material selected from the group consisting of lime and flue gas desulfurization sludge.

6. The method of claim 5 including

employing said calciferous additive in an amount of about 6 to 14 percent of the total dry mixture on a weight basis.

7. The method of claim 5 including

employing lime as said calciferous additive in an amount of about 10 to 12 percent of said dry mixture on a weight basis.

8. The method of claim 6 including

adding to said mixture of fly ash, bottom ash and calciferous additive about 5 to 15 percent water on a wet mixture weight basis.

9. The method of claim 2 including

employing about 1 to 4 to about 1 to 1 ratio of fly ash to bottom ash on a weight basis,

employing about 6 to 14 percent calciferous additive on a total mixture weight basis, and

employing about 5 to 15 percent water on a weight of wet mixture basis.

10. The method of claim 9 including

prior to said hydrothermal treatment compacting said wet mixture at a pressure of about 5,000 to 10,000 psi.

11. The method of claim 10 including

employing said method to make a building block.

12. The method of claim 10 including

effecting said hydrothermal treatment at a temperature of about 180°C to 220°C for about 4 to 8 hours.

13. The method of claim 12 including

effecting said hydrothermal treatment at a pressure of about 140 psi to 340 psi.

14. The method of claim 2 including

creating a Tobermorite crystalline phase as said mineralogical crystalline phase.

15. The method of claim 10 including

effecting said compacting in a mold having a cavity of the desired shape for about 1 second to 3 minutes.

16. The method of claim 2 including

creating by said method a building block having a compressive strength of about 2,000 to 8,500 psi.

17. The method of claim 2 including

adding to said mixture a coloring agent to produce a shaped product of the desired color.

18. The method of claim 17 including

effecting said coloring agent addition prior to blending said water into said mixture.

19. A shaped product comprising

a major portion by weight being a coal combustion ash.

said ash combined with a calciferous additive in a mineralogical crystalline phase achieved by hydrothermally treating under the influence of elevated temperature and pressure. said combustion ash calciferous additive materials admixed with water.

20. The shaped product of claim 19 including

said shaped product being a building brick having said coal combustion ash including fly ash and bottom ash.

21. The shaped product of claim 20 including

said fly ash on a weight basis being present in the ratio of about 1 to 4 to about 1 to 1 with respect to the bottom ash.

22. The shaped product of claim 20 including

said fly ash on a weight basis being present in the ratio of about 3 to 2 to about 4 to 1.

23. The shaped product of claim 21 including

said calciferous additive being present in an amount of about 6 to 14 percent of the total weight of said fly ash, said bottom ash and said calciferous additive.

24. The shaped product of claim 23 including

said calciferous additive being selected from the group consisting of lime and flue gas desulfurization sludge.

25. The shaped product of claim 24 including

said building brick having six faces each of generally rectangular configuration.

26. The shaped product of claim 24 including

said building brick being an aggregate material.

27. The shaped product of claim 24 including

said building brick being characterized by having a compressive strength of about 2,000 to 8,500 psi.

28. The shaped product of 19 including

said mineralogical crystals being of the Tobermorite type.

29. The shaped product of claim 25 including

said building blocks being characterized by having generally planar surfaces to facilitate positioning the same in an ordered array in a wall.

30. The shaped product of claim 20 including

said shaped product having a coloring agent admixed with said combustion ash.

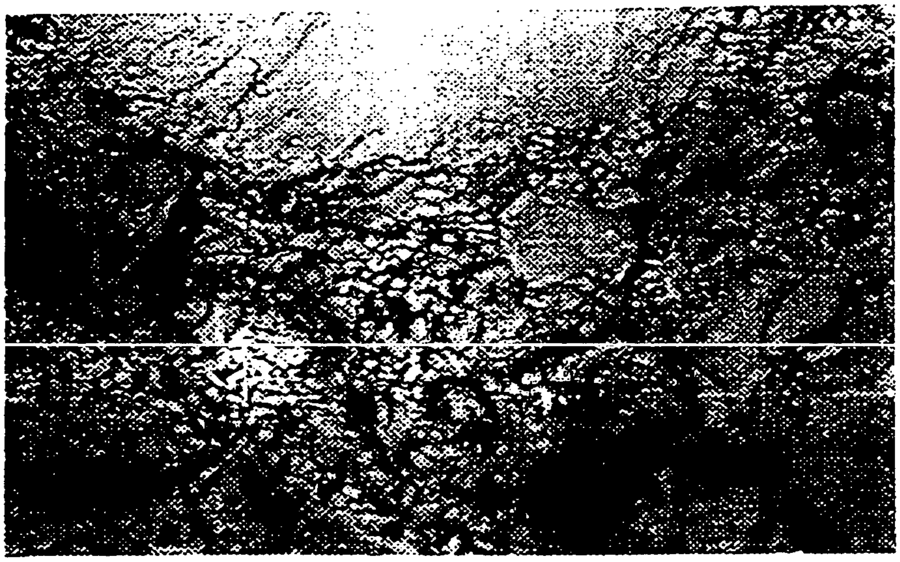

FIG. 1 PRIOR ART

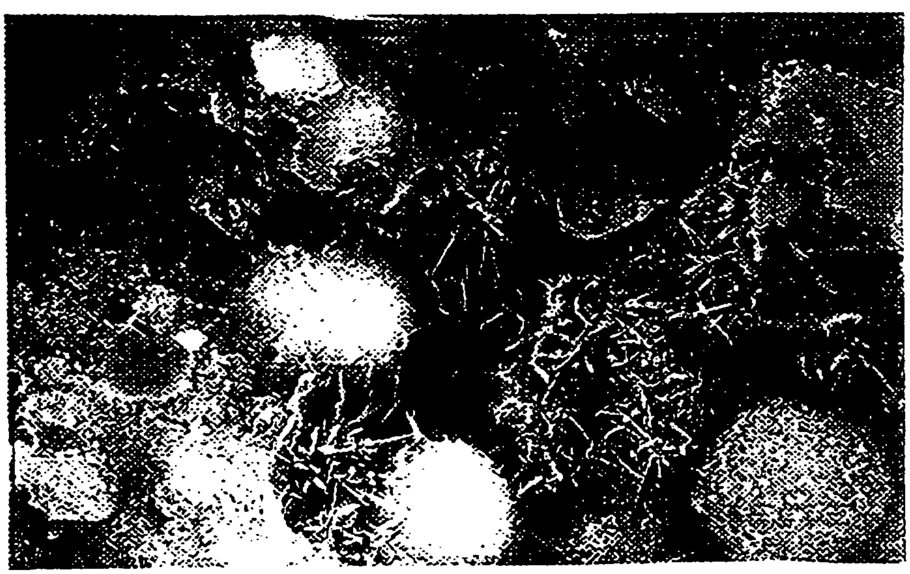

FIG. 2 PRIOR ART

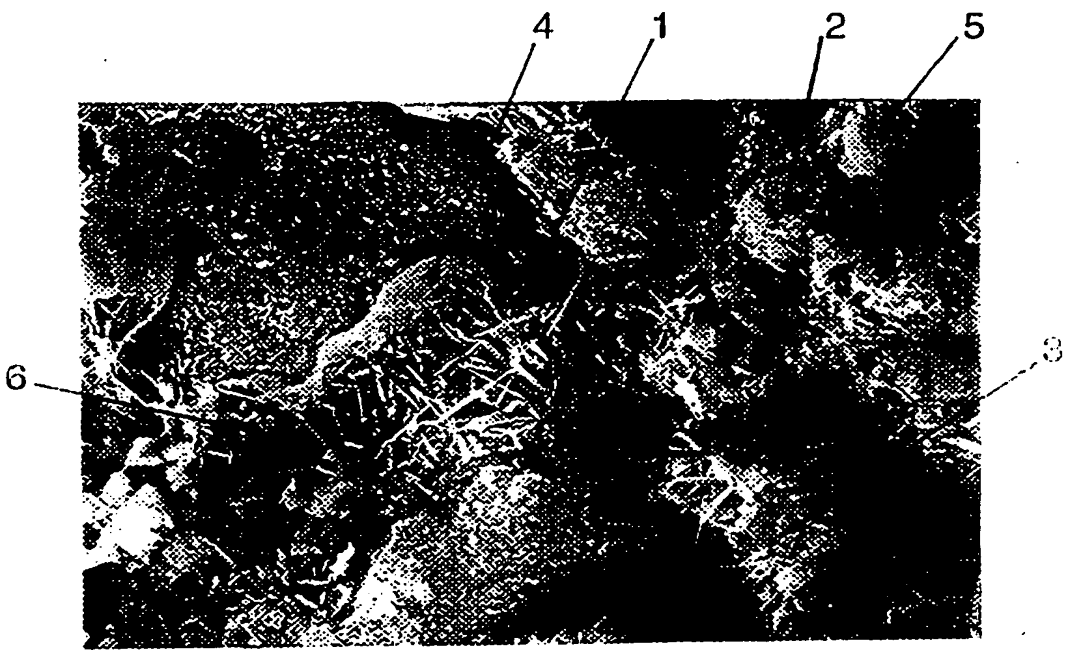

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/11754

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B28/02 C04B40/02 C04B28/18 C04B18/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 37 34 879 A (INCA BAUSTOFFTECHNIK GMBH) 23 March 1989 see page 2, line 36 - page 3, line 21 see example 1	1,10-13, 16,19,27
Y		2-5,17, 18, 20-24,30
A		6-9,14, 15,25,26
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 005, 31 May 1996 & JP 08 001126 A (NGK INSULATORS LTD), 9 January 1996, see abstract	1,19

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
31 October 1997	26. 11. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Mini, A

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/11754

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DE 43 40 786 A (MARIOTTI NORBERTO) 1 June 1995 see column 1, line 60 - column 2, line 11 see claims 1,3,6,7 ---	19
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